

PATENT SPECIFICATION

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(54) RESINS WHICH CAN BE DILUTED WITH WATER BY PROTONATION WITH ACIDS

(71) We, DR. KURT HERBERTS & CO. GmbH, vorm. OTTO LOUIS HERBERTS, D-5600 Wuppertal 2, Christbusch 25, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to resins which can be diluted with water after protonation with acids, to a process for their production and to an acid-protonated aqueous coating compositions for cathodic deposition which contains *inter alia* these resins as binders.

The production of coatings by the electrodeposition of film-forming materials onto electrically conductive metallic materials under the influence of an applied voltage has been suggested. The resins used generally consist of materials containing carboxyl groups, such as alkyd resins, acrylate resins, maleate oils, maleinised epoxy resin esters and butadiene oils which are made soluble in water by salt formation with readily volatile bases and which are deposited by the electrical current at the anode. The disadvantages of this process are that, on the one hand, the nascent oxygen formed at the anode because of the necessary deposition voltage can adversely affect the coagulated resins by oxidation and that, on the other hand, metal ions are dissolved which causes serious discoloration or even spotting of the coatings during stoving and reduces their resistance to water through salt formation.

These disadvantages can be obviated by using resins which can be deposited at the cathode. In this case, hydrogen is given off at the cathode and no metal ions are dissolved, even when the bodies consist of base metals. One of the resin systems hitherto suggested in this field is obtained by reacting anhydride-containing resins or their semiesters with diamines which contain a primary and tertiary amino group, possibly in combination with carboxyl groups as hybrid ion (H. Verdino: J. Oil. Col. Chem. Assoc. 59 (1976), 81—85). A disadvantage of this resin structure is that it involves the danger of phase separation and the migration of individual COOH-containing resin molecules to the anode which results in electrical stripping and makes the anode unuseable. By contrast, if the incorporation of carboxyl groups is avoided, there is no possibility of a crosslinking reaction with formaldehyde condensation resins and/or masked polyisocyanates because there are no suitable reactive sites present in the resin molecule. We have sought to avoid these disadvantages.

Accordingly, the present invention provides a resin which can be diluted with water after protonation with an acid, wherein the resin contains units derived from an α, β - ethylenically unsaturated dicarboxylic acid imide which form part of a polymer chain or are chemically attached to a polymer chain, and of which the imide nitrogen atoms are attached to

- a) a group containing at least one basic tertiary nitrogen atom, and

b) a group which contains a hydrogen atom reactive with formaldehyde condensation resin and/or masked polyisocyanate, the resin having an amine number of from 10 to 80 and an OH-number of from 10 to 150, the OH-groups corresponding to this OH-number optionally being completely or partly replaced by imide=NH-groups.

The present invention also provides a process for producing a resin as defined above, wherein an ethylenically unsaturated monomer, an olefin polymer oil or a condensation polymer is reacted either with (i) an α,β - ethylenically unsaturated dicarboxylic acid imide of which the imide nitrogen atom is attached to groups as defined above, or with (ii) an α,β - ethylenically unsaturated dicarboxylic acid anhydride or its semiester, and the anhydride or semiester groups of the product are converted into imide groups as defined above partly by reaction with a compound of the formula:



in which Z represents a group containing a basic tertiary nitrogen atom, and partly by reaction with at least one compound of the formula:



in which D represents a group which contains a hydrogen atom reactive with a formaldehyde condensation resin and/or masked polyisocyanate or represents a group $-\text{CONH}_2$.

The present invention further provides an acid-protonated aqueous coating composition for cathodic deposition containing binders and, optionally, pigments, fillers, corrosion inhibitors, lacquer auxiliaries and organic solvents, wherein it contains as binder

- A) a resin as defined above,
- B) at least one formaldehyde condensation resin and/or masked polyisocyanate, the quantitative ratio of component A to component B being from to 95:5 to 50:50 (% by weight), based on resin solids, and
- C) from 0 to 30 parts by weight of a resin containing a hydroxyl group, based on 100 parts by weight of the sum of components A and B (based on solids).

Groups which contain at least one basic tertiary nitrogen atom are preferably those which contain from one to three and, with particular preference, one basic tertiary nitrogen atom.

The resins of the present invention are thus distinguished by the following:

1. The introduction of basic N-groups, for example by reacting anhydride-containing resins with dialkylaminoalkylamines, dialkylamino arylamines or dialkyl hydrazines.
2. The incorporation of crosslinkable sites, such as OH-groups, through hydroxyalkylimides and/or of acid NH-groups through cyclic imides.
3. The selection of the suitable characteristics of the cathodically depositable resin, such as its viscosity (molecular weight), amine number, number of crosslinking sites, neutralising agent and degree of neutralisation.
4. Thermal crosslinking with water-soluble cationic and/or water-insoluble formaldehyde condensation resins, the reaction being activated by the acid NH-group or residual COOH-groups, possibly with addition of resins containing hydroxyl groups.
5. Thermal crosslinking with mixed-in masked polyisocyanates. After the electrophoretic coating, the protective group is eliminated during stoving and reacts with the functional groups present, optionally in the presence of catalysts, to form a hard film.

In one preferred process for producing the coating composition of the present invention, a part of component A is ground with pigments, fillers, corrosion inhibitors, lacquer auxiliaries and/or organic solvents and subsequently mixed with the other constituents of the coating composition. The part of component A which is ground with the pigments etc. may already be protonated with acid and water may be added as liquid medium. However, it is also possible to grind the non-protonated component A in an organic solvent as liquid medium.

The production of resins which contain α,β - ethylenically unsaturated dicarboxylic acid anhydrides as part of a polymer chain or chemically attached to

the polymer chain is known *per se*. The resins are formed for example by addition reactions (substituting addition by a hydrogen atom migrating, Diels-Alder reaction) of unsaturated dicarboxylic acid (anhydrides) with unsaturated fatty acid esters or olefin polymer oils or by the copolymerisation of unsaturated dicarboxylic acid (anhydrides) with other unsaturated monomers. Maleic acid anhydride is preferred both according to the prior art and according to the invention. The maleic acid anhydride may be used in a concentration of from 5 to 30% by weight. The quantity is determined by the further reaction steps.

The unsaturated starting materials for the addition reaction may be obtained from natural unsaturated oils or may be produced by the complete esterification of conjugated or isolated unsaturated fatty acids with polyalcohols, such as pentaerythritol or trimethylol propane, optionally modified with aromatic carboxylic acids or colophony. The polyols used may also be polyglycidyl ethers of the 2,2-bis-(4-hydroxyphenyl)-propane type or epoxide novolak, polyglycidyl amines, glycidyl(meth)acrylate copolymers or polyalkadiene epoxides and also copolymers containing OH-groups, such as styrene/allyl alcohol or methyl methacrylate/hydroxyethylacrylate copolymers. The olefin polymer oils are polybutadiene oils or polypentadiene oils with various steric configurations (1,4-cis, 1,4-trans or 1,2-vinyl) which may be additionally copolymerised with other unsaturated monomers, such as styrene, (meth)acrylic acid esters or other vinyl compounds. The chain ends may contain carboxyl groups or amino groups emanating from chain terminators. The resin to be maleinised may be blended before-hand with up to 30% by weight of cyclopentadiene resin, coumarone-indene resin, degraded rubber or cyclo rubber.

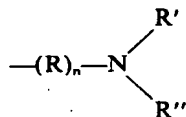
The unsaturated dicarboxylic acid anhydrides used may be maleic acid anhydride, itaconic acid anhydride, citra-conic acid anhydride, dimethyl maleic acid anhydride or α,β -unsaturated dicarboxylic acids, such as fumaric acid, maleic acid or mesaconic acid, in whose case water may be split off with closure of the ring after the addition reaction or during the further reaction with amino compounds. Maleic acid anhydride is preferably used. Maleic imide may also be used as addition component. The reaction takes place at 190 to 240°C in an inert gas and may be carried out in the presence of solvents, such as commercial-grade xylene and/or in the presence of radical inhibitors such as sterically hindered phenols, secondary arylamines, *p*-phenylene diamine derivative or phenothiazine.

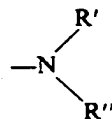
Anhydride-containing copolymers are obtained by the radical or ionic solution copolymerisation of unsaturated dicarboxylic acid (anhydrides) with (meth)acrylic acid esters, styrene or styrene derivatives and/or other copolymerisable unsaturated compounds, such as vinyl ethers, vinyl ketones, vinyl esters, allyl esters or even ethylene. The reaction temperature has to be co-ordinated with the decomposition temperature of the catalyst added and the addition of polymerisation regulators is possible. In order to keep the anhydride structure intact, the solvent used is generally a solvent free from hydroxyl groups, such as methyl isobutyl ketone, cyclo-hexanone or xylene which has to be distilled off again after the imide-forming reaction. However, depending upon the other reaction conditions selected, the use of alcoholic solvents, such as butyl glycol, need not have a troublesome effect because the semiesters formed can also further react by transamidation. For this reason, the preferred maleic acid anhydride may also be replaced as comonomer by corresponding semiesters, particularly those with lower aliphatic monoalcohols or monoglycol ethers having 1 to 6 carbon atoms, for example maleic acid monomethyl ester.

The anhydride-containing resins are reacted either directly or after the previous formation of a monoalcohol semiester by the dropwise addition of, for example, dialkyl-amino-alkylamines, dialkylamino arylamines or dialkyl hydrazines, at temperatures of from 60 to 180°C and preferably at temperatures of from 90 to 130°C in the presence of 10% by weight of commercial-grade xylene, the water eliminated being azeotropically removed from the circuit.

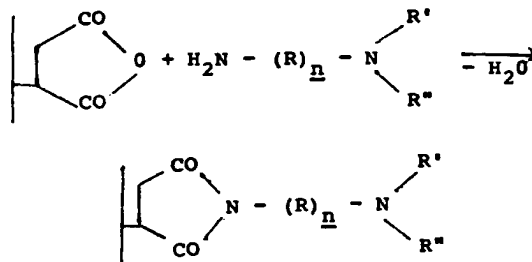
The reaction with dialkylaminoalkylamines is preferred.

In the following formula scheme, the groups

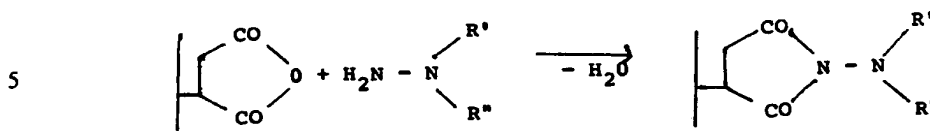




correspond to the symbol—Z in formulae (I) and (III).



For example, $\text{R} = \text{---}(\text{CH}_2)\text{---}$, R' and $\text{R}'' = \text{---CH}_3$ or $\text{---C}_2\text{H}_5$, and $n=2$ to 6 .

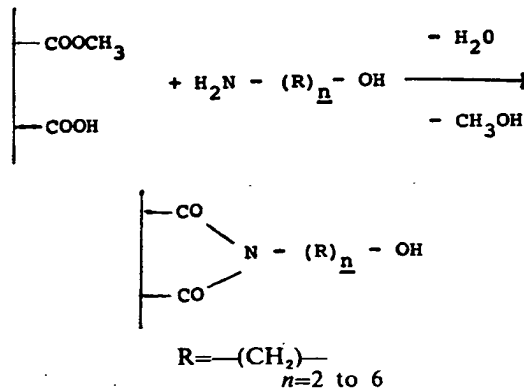


The quantity of amine used is determined by the amine number to be produced in the product, the dialkylamino group only acting as residual basic constituent on completion of the reaction. An amine number of 20 to 80 is sufficient for the production of a water-soluble resin. The dialkylamino component used may be dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminocyclohexylamine, N,N - diethyl - *p* - phenylene diamine, N,N - dimethylxylylene diamine, bis - (dimethylamino) - propylamine, tris - (dimethylamino) - ethyl - amine, cyclohexylaminoethylamine, phenyl methylaminoethylamine, 2 - [β - aminoethyl] - pyridine or N - (2 - aminoethyl) - morpholine.

In addition, functional groups have to be incorporated for crosslinking with formaldehyde condensation resins and/or masked polyisocyanates. According to the invention, this may be achieved by:

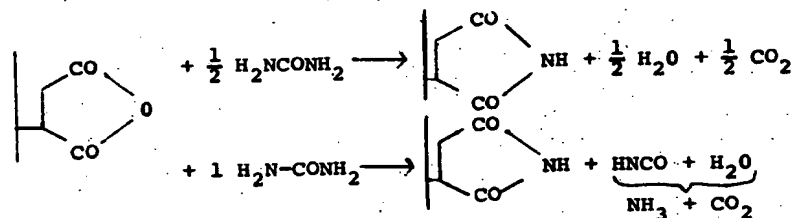
1. Converting existing carboxyl groups or their anhydrides or semiesters into hydroxy-functional compounds by the addition of monoepoxides, such as propylene oxide, or preferably by reaction with hydroxy alkylamines or hydroxy arylamines.

In the following two formula schemes, the groups $\text{---}(\text{R})_n\text{---OH}$ and ---H correspond to the symbol —D in formulae (II) and (IV):



This reaction may be carried out in admixture or in steps and *in vacuo* at temperatures of from 40 to 180°C and preferably at temperatures of from 60 to 160°C. Crosslinking reactions complicate the reaction with increasing number of OH-groups per amino alcohol. In order to avoid gel formation, it is advisable to use the methanol or butanol semiester rather than the anhydride as starting product. In addition, the reaction temperature should only be increased from 60 to 70°C after complete transamidation in order to obtain ring closure. The aminoalcohol used may be monoethanolamine, monoisopropanolamine, 2-amino-2-methyl propanol, 2-amino-2-methyl-1,3-propane diol, 2-amino-1-butanol, tris-(hydroxymethyl)-aminomethane, "diglycolamines", such as 2-(2-aminoethoxy)ethanol, aminocyclohexanol or *p*-aminophenol.

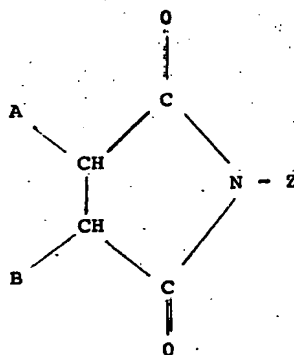
2. Converting existing anhydride groups into cyclic imides by boiling with gaseous ammonia or compounds which liberate ammonia such as, for example, ammonium carbonate or urea at a temperature of 80°C or more and, more especially, at a temperature of 120°C or more, the water eliminated being azeotropically removed from the circuit. Where ammonium carbonate or urea is used, the reaction is over when no more carbon dioxide is given off. Finally, any residual water of reaction is distilled off *in vacuo* with the solvent:



The imide groups formed are acid in character and, in the deposited mixture with formaldehyde condensation resins, act not only as a reactive crosslinking site, but also catalytically on the reaction with the OH-groups by virtue of their acid character. In order to overcome the high viscosities formed hydrogen bridges during the production process, it is possible in this case, too, to transesterify methanol semiester with urea or to transamidate maleic imides adducts with dialkylaminoalkylamines.

According to the invention, particularly preferred resins are those which contain in co-condensed form

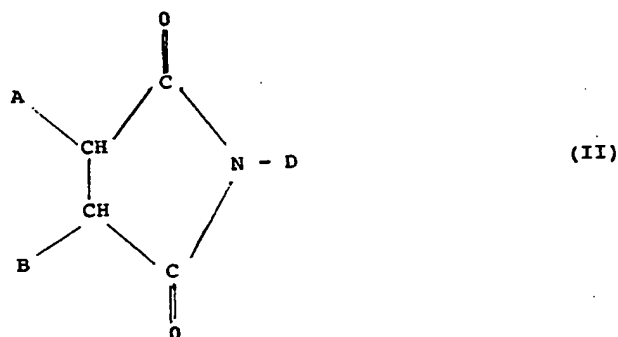
a) the group:



(I)

which through A and B or A alone, when B is a hydrogen atom, forms part of a copolymer, an olefin polymer oil or a condensation polymer which is suitable for use as film former, and Z represents a group which contains at least one basic tertiary nitrogen atom,

b) and the group:



in which A and B may have the same meaning as in formula (I) and D represents a group which contains a hydrogen atom reactive with formaldehyde condensation resins and/or masked polyisocyanates. NH-Imide resins are preferred for combination with masked polyisocyanates.

Other preferred resins are those which contain dicarboxylic acid imides added with 1,4 - cis - polybutadiene oil with a molecular weight of from 1000 to 4000. In their case, too, maleic acid imide is preferably used as the dicarboxylic acid imide. In practice, it is possible to use combinations with amine numbers of from 10 to 80, more especially from 20 to 60 (DIN 53 176) and hydroxyl numbers of from 10 to 150, more especially from 20 to 100 (DIN 53 240), the OH-groups corresponding to this OH-number being completely or partly replaceable by imide=NH-groups. The viscosity of the polymer oil adducts or polycondensates according to the invention, in the form of 60% solutions in butyl glycol at 25°C, is preferably from 500 to 5000 m Pas and, with particular preference, from 1000 to 3000 m Pas. The viscosity of the copolymers according to the invention in the form of 60% solutions in dimethyl formamide at 25°C is preferably from 500 to 6000 m Pas and, with particular preference, from 2000 to 5000 m Pas. These viscosities are obtained by a suitable choice, of the starting products, for example the polymer oils or polycondensates with correspondingly high viscosities used as starting products, the reaction times and the concentrations, particularly of the α,β -unsaturated dicarboxylic acid anhydrides or their derivatives. In order to obtain high coverage (=high deposition voltage), it is desirable to have as high a viscosity (=molecular weight) as can be tolerated without any adverse effect upon levelling.

The formaldehyde condensation resin used may be selected from water-soluble and water-insoluble urea, benzoguanamine or melamine-formaldehyde resins, phenol resols, such as non-plasticised, optionally etherified cresol resols or bisphenol - A - resols which may optionally be modified with a proportion of alkyl phenol, or unsaturated phenol resol ethers, such as Methylon (Trade Mark) resin 75 108 or 2 - chloroallyl methylol phenol ether.

In order to make the resins soluble in water, hexamethylol melamine resins may be directly reacted with secondary amines or fully etherified trimethylol melamine resins may be reacted with secondary amines under hydrolytic conditions. In the case of the phenolic resins, basic groups are introduced by Mannich condensation with secondary amines (alkyl or hydroxyalkyl-amines) and formaldehyde or formaldehyde donors. The number of amino groups does not have to be so high that the crosslinking agent completely dissolves in the protonated solution. It is sufficient for the amino groups to be present in the quantity which enables the resin to be satisfactorily emulsified in the water-soluble carrier resin.

The masked polyisocyanate is obtained by reacting stoichiometric quantities of polyisocyanate and monofunctional compound with active hydrogen. Suitable masking agents are, for example, phenols, lactams, oximes, acetoacetic ester, thiophenols, phthalimide, imidazole, acetyl acetone and malonic esters. Caprolactam is preferably used as the masking agent. The blocked isocyanates formed have to be stable in aqueous solution at a substantially neutral to weakly acid pH - value and must split back again at suitable stoving temperatures of from 170 to 200°C.

Products such as these are marketed by several companies, for example Desmodur (Trade Mark) CT-stabil (a product of Bayer AG), Additol VXL 80/81 (a product of Hoechst AG), Neorez SC 33 (a product of Polyvinyl-Chemie).

When protective groups which contain additional water-solubilising basic

groups, such as N - dialkyl - aminophenols or N - dialkylaminoketoximes of dialkylamino alcohols, are used, the solubility of the masked polyisocyanates, in water is improved and the hydrophilic nitrogen atom is removed from the film with the protective group during stoving. Typical polyfunctional isocyanates are aliphatic isocyanates, such as hexylene diisocyanate or the biuret of trimethylene diisocyanate, aromatic isocyanates such as toluene diisocyanates, or diphenyl methane diisocyanate or cycloaliphatic isocyanates, such as isophorone diisocyanate or dicyclohexyl methane diisocyanate. Reaction products of a diol with 2 moles of a diisocyanate or of 1 mole of triol with 3 moles of a diisocyanate are used for producing isocyanate-containing prepolymers of relatively high molecular weight.

The ratio of the cathodically depositable resins (component A) to the crosslinking agent (component B) is from 95:5 to 50:50 (% by weight) and preferably from 90:10 to 60:40 (% by weight), based on resins solids. These systems are hardened by stoving for 15 minutes to 1 hour at 160 to 210°C. In addition to the crosslinking reaction a polymerisation reaction involving the unsaturated double bonds still present in the resin may also take place. Component B is best incorporated by mixing the resins as concentrates, protonating them together and then diluting them with water.

In order to accelerate oxidation with air and/or to catalyse the demasking process or the reaction of the free isocyanate, metal siccatives, such as iron naphthenate, cobalt octoate, lead naphthenate, zinc octoate or dibutyl tin dilaurate, are added, the synergistic accelerating effect of the amino groups in the resin being additionally utilised.

The usual additions are generally from 0.1 to 1% by weight, based on resin solids.

In order to enable a better hardness-elasticity ratio to be adjusted and the dispersibility properties to be positively influenced, up to 30% by weight and preferably up to 20% by weight of resins containing hydroxyl groups (component C) may be added. Suitable resins of this type are oil-like esters of polyalcohols which still contain from 1 to 2 hydroxyl groups in the molecule, elastic chainlike compounds which predominantly contain terminal, primary hydroxyl groups or aryl copolymers containing OH-groups. The following are examples of such compounds:

1. Esters of polyols, such as glycerol, trimethylol propane, penta-erythritol or ester amides of hydroxyalkylamines with synthetic or natural, saturated or dry monofatty acids, such as isononanoic acid, first runnings coconut oil fatty acid, hydroxy stearic acid, soya fatty acid, tall oil fatty acid, linseed oil fatty acid or synouric fatty acid.

Transesterification is carried out completely and the quantitative ratios are selected in such a way that at least one hydroxyl group remains free in the molecule and at least one hydroxyl group or amino group is esterified.

2. Hydroxy - group - containing reaction products of polyglycidyl ethers, such as liquid epoxy resins, with synthetic or natural saturated or air-drying fatty acids such as defined in 1) above, the fatty acid being added in such a quantity that all the epoxy groups are reacted. In one particular embodiment, solid poly glycidyl ethers, such as Epikote (Trade Mark) 1004, are used for the reaction with alkanolamines which contain an epoxy-reactive NH-group, such as diethanolamine, diisopropanolamine, isopropanolamine or N - cyclohexyl ethanolamine. The reaction conditions are selected in such a way that, although all the epoxy groups are split up, sufficient hydroxyl groups remains present for a further reaction.

3. Esters of aliphatic dicarboxylic acids, such as adipic acid or sebacic acid, with glycols, polyalcohols which contain more than 2 hydroxyl groups, or hydroxy alkylamines, 1 mole of glycol, polyalcohol or amino alcohol being reacted per carboxyl group.

4. Reaction of caprolactam with polyalcohols, such as ethylene glycol or trimethylol propane to form caprolactam polyols.

5. Copolymers containing hydroxyl groups which are formed by the reaction of OH-functional unsaturated monomers, such as allyl alcohol or hydroxy alkyl (meth) acrylates, with styrene, vinyl toluene or (meth) acrylic acid esters, optionally with addition of unsaturated basic monomers, such as dialkylaminoalkyl (meth) acrylic acid esters.

Suitable hydroxyl - group - containing resins (component C) have an OH - number

of from 100 to 900, preferably from 150 to 500, and an average molecular weight of from 100 to 3000, preferably from 400 to 2000. The complete esterification of the starting components ensures that the acid number of these substances is below 5 and preferably below 2. The resins must be in a molecular-weight range in which they are no longer volatile during stoving, but assume an improved fluidity for good film formation. The resins may assume a certain solubility in water in acid medium through an amine number below 60 and, more especially, below 30. However, it is sufficient for polar groups to be present in the quantity which enables the resin to be satisfactorily emulsified in the water-soluble carrier resin. The production of suitable hydroxyl - group - containing resins is known and is carried out in the usual way by azeotropic or melt condensation of the starting products or by solution polymerisation of the monomers.

These resins are best incorporated by mixing them in liquid form with the other concentrate, protonating them together and then diluting them with water. If the resin is not completely liquid, it may be dissolved in as high a concentration as possible in alcoholic or glycolic solvents.

The solubility in water is obtained by salt formation of the resin containing amino groups with acid compounds. Acids suitable for this purpose are, for example, hydrochloric acid, phosphoric acid, boric acid, formic acid, acrylic acid, acetic acid, malonic acid, dimethylol propionic acid, citric acid, lactic acid and malic acid. In order to obtain high bath conductivity and good film properties, it is preferred to use acids with as low a molecular weight as possible or a small solvation shell and acids which decompose into gaseous products when the film is stoved. Any unreacted carboxyl groups formed by incomplete reaction of the anhydride or semiester with amines, by α,β - unsaturated monocarboxylic acids introduced during synthesis of the resin or by chain termination with carbon dioxide may support the crosslinking reaction with formaldehyde condensation resins by their catalytic effect and, at the same time, provide the resin with a certain degree of solubility in water. It has been found to be of advantage in some cases for the resin to contain a small number of carboxyl groups. At all events, however, the number of carboxyl groups should not be excessively high because they can give rise to a deterioration in the quality of the film. When the resins are combined with masked isocyanates, carboxyl groups should be avoided in the film because the basic amino groups have a greater catalytic effect.

Water-dilutable resins are obtained by protonation with acids by adding to the basic resin from 0.2 to 1.3 equivalents and preferably from 0.4 to 1.0 equivalent of the acid compound, based on the basic nitrogen atom in the resin, and thoroughly stirring the mixture at temperatures of from 20 to 90°C.

The bath of coating composition may contain up to 15% by weight of organic solvents in order to reduce its viscosity, to control the deposition voltage and to improve levelling. The organic solvents used may be water-soluble solvents, such as alcohols, glycol ethers, keto alcohols and also small quantities of water-insoluble solvents, such as hydrocarbons of different chain length. The aqueous bath has a solids content of from 5 to 30% by weight, preferably from 10 to 20% by weight. The bath has a pH-value of from 4 to 8, preferably from 5 to 7. In order to obtain high coverage, the conductivity of the bath should be as high as possible, for example in excess of $1000 \mu\text{scm}^{-1}$ and more especially in excess of $1500 \mu\text{Scm}^{-1}$. The conductivity of the bath may optionally be increased by the addition of salts of tertiary amines which contain at least one long-chain carbon chain as alkyl radical, of the type which may be obtained from dimethyl soya amine and formic acid. The anodes used are electrically conductive and non-corroding electrodes, of for example stainless steel or graphite. The article to be cathodically coated and the anode are immersed in an aqueous bath in the same way as hitherto known for electrophoretic deposition. During the deposition process, the bath is best kept at temperatures of from 20 to 35°C. The voltage to be applied is preferably from 20 to 500 volts and most preferably from 200 to 400 volts. The viscosity of the resin, its solids content, the deposition temperature, time and voltage are selected in such a way that the required layer thickness on the sheet metal substrate is obtained after flushing and stoving.

The concentrates with a solids content of from 85 to 60% by weight may be pigmented in the usual way, for example in a ball mill, on a three-roll stand or in a sand mill and may be processed by any of the usual coating techniques (spread-coating, roll-coating, spray-coating, dip-coating) after dilution to the processing consistency. During grinding in the presence of formaldehyde condensation resins and/or masked polyisocyanates or components containing hydroxyl groups, a

partial crosslinking reaction can be produced solely by the increase in temperature of the highly viscous products, resulting in a deterioration in the stability of the bath and in inadequate levelling of the deposited film. Accordingly, it is best to grind part of component A with pigments, fillers, corrosion inhibitors, lacquer auxiliaries and/or organic solvents and then to mix it with the other constituents. These other constituents may then be cold-mixed with component A.

It is possible to use any of the usual pigments, fillers, corrosion inhibitors and lacquer auxiliaries, such as anti-foaming agents or metal siccatives, providing they do not enter into any troublesome reactions with water in the acid pH-range, do not entrain any water-soluble foreign ions and are not precipitated on ageing. The lacquers are particularly suitable for the electro - dip - lacquering of metals and produce smooth, hard films with high bond strength and elasticity, coupled with high resistance to corrosion and detergents, for example after stoving for 30 minutes at 180°C. The pigment-binder ratio is dependent upon the viscosity of the binder and is generally from 0.15:1 to 0.5:1.

The invention is further illustrated by the following Examples.

EXAMPLE 1

936 g of a 1,4 - cis - polybutadiene oil with an average molecular weight of 1500, 100 g of commercial-grade xylene and 1.2 g of a standard commercial-grade antiager of the diarylamine type were heated under nitrogen to a temperature of 140°C in a two litre flask. Following the addition of 264 g of maleic acid anhydride, the temperature was increased to 195°C and was kept at that level until no more free maleic acid anhydride could be detected. After cooling to 90 to 100°C, 93.6 g of dimethylaminopropylamine were added dropwise over a period of 30 minutes, after which the temperature was kept at that level for 1 hour and subsequently increased to 160°C. When there was no further reduction in the acid number measured using aqueous KOH, 53.4 g of urea were carefully scattered in in the form of very small portions. The xylene removed any water formed during the reaction from the circuit. When foaming abated, the temperature was increased to 190°C and a vigorous stream of nitrogen was introduced until no more carbon dioxide could be detected with barium hydroxide solution. The solvent was then distilled off *in vacuo*, followed by dilution with butyl glycol to 90% by weight.

Viscosity: 1400 m Pas (as measured on a 60% solution in butyl glycol at 25°C)

Amine number: 40 mg KOH per g of solids (measured with aqueous HCL).

Refill concentrate:

1390 g of the resin obtained as described above were mixed with 250 g of a 75% etherified bisphenol - A - resol in isopropanol and 180 g of a 70% adduct of Epikote 1007 with diethanolamine. This adduct was produced by reacting 1 mole of diethanolamine per epoxy group in the presence of a little triphenyl phosphine as catalyst and diluted (1:1) in butyl glycol-Sektol.

Solid content: 85.6% by weight (measured by heating for 40 minutes to 180°C in a recirculating air drying cabinet).

Deposition bath:

200 g of solids of the refill material were gradually diluted with 3.7 g of formic acid and with distilled or deionised water until 2 liters of solution were formed. MEQ-S-value: 40 (milliequivalents of acid per 100 g of solid resin)

Solids content: 10% by weight (measured by heating for 15 minutes to 185°C in a recirculating air drying cabinet).

The diluted bath was stirred for 24 hours. The deposition voltage on Bonder 127 sheets amounted to 200 volts for a dry film thickness of 25 μ m. The film deposited in 2 minutes at 30°C was stoved for 30 minutes at 175°C after flushing with water. The following characteristics were measured:

pH-value	5.7
bath conductivity	930 μ Scm ⁻¹
pendulum hardness (Konig)	70 s
Erichsen indentation	8.8 mm

EXAMPLE 2

240 g of butyl glycol were heated in an inert gas to a temperature of 130°C in a 2 litre flask. A mixture of 209 g of maleic acid anhydride, 730 g of butyl acrylate,

261 g of styrene and 14.4 g of azo - bis - isobutyronitrile was then run in with stirring over a period of 3 hours, after which another two batches of 3.6 g of azo - bis - isobutyronitrile were added at intervals of 30 minutes. The mixture was then left to react for 2 hours at a temperature of 130°C. After cooling to 70°C, 80 g of methanol were added with 1 ml of triethylamine. This temperature was maintained for 1 hour and then increased to 140°C. When there was no further reduction in the acid number as measured with aqueous KOH, 19.2 of urea were scattered in, in the form of very small portions. When foaming abated, the temperature was increased to 160°C and a vigorous stream of nitrogen was introduced until no more carbon dioxide could be detected with barium hydroxide solution. The mixture was then cooled to 90°C and a mixture of 65.5 g of dimethylaminopropylamine and 52.3 g of monoethanolamine was added dropwise over a period of 30 minutes. The temperature was kept at 90°C for 1 hour and then increased to 160°C where it was kept until there was no further reduction in the acid number.

Viscosity: 3600 m Pas (as measured on a 60% solution in dimethyl formamide at 25°C)

Amine number: 30 mg of KOH per g of solids (as measured with aqueous HCl)

Solids content: 83.9% by weight (as measured by heating for 40 minutes to 180°C in a recirculating air drying cabinet)

Refill concentrate:

1350 g of the resin obtained as described above were mixed with 225 g of a 75% etherified bisphenol - A - resol in isopropanol and diluted with isopropanol to a solids content of 80% by weight.

Solids content: 80% by weight.

Deposition bath:

200 g of solids of the refill material were gradually diluted with 4.8 g of acetic acid and distilled or deionised water until 2 litres of solution were formed.

MEQ-S-value (milliequivalents of acid per 100 g of solid resin): 40

Solids content: 10% by weight (measured by heating for 15 minutes to 185°C in a recirculating air drying cabinet).

The diluted bath was stirred for 24 hours. The deposition voltage on Bonder 127 sheets amounted to 250 volts for a dry film thickness of 25 μ m. The film deposited in 2 minutes at 30°C was stoved for 25 minutes at 200°C after flushing with water. The following characteristics were measured:

pH-value	5.5
Conductivity	1350 μ Scm ⁻¹
pendulum hardness (Konig)	145 s
Erichsen indentation	9.6 mm.

EXAMPLE 3

The resin formulation and procedures were as in Example 1, except that the resin was diluted to 80% by weight with butyl glycol and secondary butanol (2:1) after the solvent had been distilled off.

Deposition bath:

170 g of solids of the resin concentrate were mixed with 30 g of isophorone diisocyanate which was masked with caprolactam and dissolved to form a 90% solution in butyl glycol, and 2.5 g of zinc Soligen (Trade Mark), containing 8% of zinc, and the resulting mixture was then gradually diluted with 5.4 g of 85% formic acid and distilled or deionised water until 2 litres of solution were formed.

MEQ-S-value 50

Solids content 10% by weight.

The diluted bath was stirred for 24 hours. The deposition voltage on Bonder 125 sheets amounted to 100 volts for a dry film thickness of 22 mm. The film deposited in 2 minutes at 25°C was stoved for 25 minutes at 190°C after flushing with water. The following characteristics were measured:

pH-value	5.3
bath conductivity	1300 μ Scm ⁻¹

	pendulum hardness		
	(Konig)	65 seconds	
	ASTM (DIN 50 021)		
5	168 hours on bright sheet	HST 2 to 6 mm	5
	360 hours on Bonder 125	HST 2 to 3 mm	

EXAMPLE 4

The procedure was as in Example 1, except that the following quantities of material were used:

10	1070 g of a polybutadiene oil with an average molecular weight of 100 (40 to 45% 1,2-vinyl, 30 to 35% 1,4-trans, 25 to 30% 1,4-cis-configuration)	10
	1.4 g of antiager of the diarylamine type	
	328 g of maleic acid anhydride	
	155 g of commercial-grade xylene	
15	134 g of dimethylaminopropylamine	15
	61 g of urea	

Dilution 85% by weight with butyl glycol.

End values measured:

	Viscosity=930 m Pas (as measured on a 60% solution in butylglycol at 25°C)	
20	Amine number=50 mg KOH per g of solids	20
	Solids content=88% by weight (40 minutes at 180°C).	

Deposition bath:

The following solutions were mixed:

25	193 g of basic resin solution (solids content 88% by weight in butyl glycol)	25
	22.2 g of Desmodur (Trade Mark) N-solution masked with caprolactam (solids content=90% by weight in butyl glycol)	
	15.3 g of styrene/allyl alcohol copolymer solution with a molecular weight of 1700 and an OH-number of 250 (solids content=65% by weight in secondary butanol)	
	5.4 g of 85% formic acid, and	

30	diluted with distilled or deionised water until 2 litres of solution were formed.	30
	MEQ-S-value 50.	
	Solids content 10% by weight.	

35	The diluted bath was stirred for 24 hours. The deposition voltage on Bonder 127 sheets amounted to 100 volts for a dry film thickness of 25 μ m. The film deposited in 2 minutes at 30°C was stoved for 25 minutes at 190°C after flushing with water.	35
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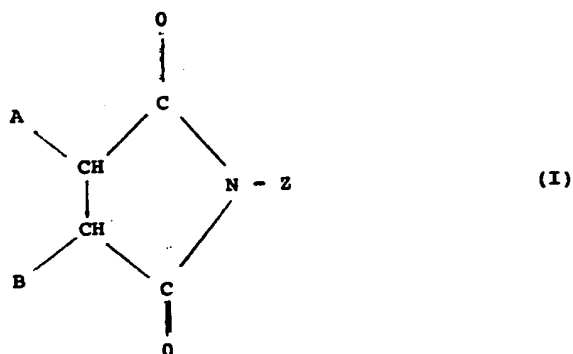
The following characteristics were measured:

40	pH-value	5.0	
	bath conductivity	1090 μ S cm^{-1}	
	pendulum hardness		40
	(Konig)	91 seconds	
	Erichsen indentation	8.2 mm.	

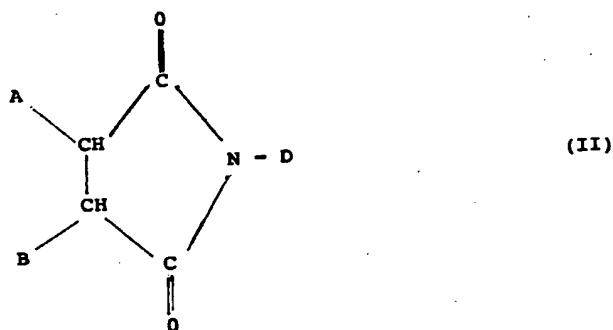
WHAT WE CLAIM IS:—

45	1. A resin which can be diluted with water after protonation with an acid, wherein the resin contains units derived from an α,β - ethylenically unsaturated dicarboxylic acid imide which form part of a polymer chain or are chemically attached to a polymer chain, and of which the imide nitrogen atoms are attached to	45
	a) a group containing at least one basic tertiary nitrogen atom, and	
50	b) a group which contains a hydrogen atom reactive with formaldehyde condensation resin and/or masked polyisocyanate,	50
	the resin having an amine number of from 10 to 80 and an OH-number of from 10 to 150, the OH-groups corresponding to this OH-number optionally being completely or partly replaced by imide=NH-groups.	
55	2. A resin as claimed in claim 1, wherein the amine number is from 20 to 60.	55
	3. A resin as claimed in claim 1 or 2, wherein the OH-number is from 20 to 100.	

4. A resin as claimed in any of Claims 1 to 3, wherein the resin contains
a) a group of the formula:



5. which through A and B or A alone, in which case B represents a hydrogen atom, form part of a copolymer, an olefin polymer oil or a condensation polymer which is suitable as film former, and Z represents a group containing a basic tertiary nitrogen atom, and
b) a group of the formula:



10. in which A and B have the same meaning as for formula (I) and D represents a group which contains a hydrogen atom reactive with a formaldehyde condensation resin and/or masked polyisocyanate.
15. 5. A resin as claimed in Claim 4, wherein the polymer oil adduct or condensation polymer has a viscosity of from 500 to 5000 mPas (millipascals) as measured on a 60% solution in butyl glycol at a temperature of 25°C.
20. 6. A resin as claimed in claim 5, wherein the viscosity is from 1000 to 3000 mPas.
25. 7. A resin as claimed in Claim 4, wherein the copolymer has a viscosity of from 500 to 6000 mPas, as measured on a 60% solution in dimethyl formamide at a temperature of 25°C.
30. 8. A resin as claimed in Claim 7, wherein the viscosity is from 2000 to 5000 mPas.
9. A resin as claimed in any of Claims 1 to 8, wherein the resin contains the dicarboxylic acid imide units chemically attached to 1,4 - cis - polybutadiene oil with an average molecular weight of from 1000 to 4000.
10. A resin as claimed in claim 1 substantially as herein described with reference to any of the Examples.
11. A process for producing a resin as defined in any of Claims 1 to 10, wherein an ethylenically unsaturated monomer, an olefin polymer oil or a condensation polymer is reacted either with (i) an α,β - ethylenically unsaturated dicarboxylic acid imide of which the imide nitrogen atom is attached to groups as defined in claim 1, or with (ii) an α,β - ethylenically unsaturated dicarboxylic acid anhydride or its semiester, and the anhydride or semiester groups of the product are

converted thereafter into imide groups as defined in claim 1 partly by reaction with a compound of the formula:



in which Z has the same meaning as defined in claim 4, and partly by reaction with at least one compound of the formula:



in which D has the same meaning as defined in claim 4, or represents a group $-\text{CONH}_2$.

12. A process as claimed in Claim 11, wherein the α,β - unsaturated dicarboxylic acid derivative used is the corresponding maleic acid derivative.

13. A process as claimed in claim 11 or 12, wherein the quantitative ratios between the starting products, the viscosity of the polymer oil or condensation polymer used and the reaction time are selected in such a way that the polymer oil adduct or condensation polymer obtained has a viscosity of from 500 to 5000 mPas, as measured on a 60% solution in butyl glycol at a temperature of 25°C.

14. A process as claimed in claim 13, wherein the viscosity is from 1000 to 3000 mPas.

15. A process as claimed in claim 11 or 12, wherein the quantitative ratios between the starting products and the reaction times and conditions are selected in such a way that the copolymer formed has a viscosity of 500 to 6000 mPas, as measured on a 60% solution in dimethyl formamide at a temperature of 25°C.

16. A process as claimed in claim 15, wherein the viscosity is from 2000 to 5000 mPas.

17. A process as claimed in claim 11 substantially as herein described with reference to any of the Examples.

18. A resin whenever produced by a process as claimed in any of claims 11 to 17.

19. An acid-protonated aqueous coating composition for cathodic deposition containing binders and, optionally, pigments, fillers, corrosion inhibitors, lacquer auxiliaries and organic solvents, wherein it contains as binder

A) a resin as defined in any of claims 1 to 10,

B) at least one formaldehyde condensation resin and/or masked polyisocyanate, the quantitative ratio of component A to component B being from 95:5 to 50:50 (% by weight), based on resin solids, and

C) from 0 to 30 parts by weight of a resin containing a hydroxyl group, based on 100 parts by weight of the sum of components A and B (based on solids).

20. A composition as claimed in claim 19, wherein the ratio of component A to component B is from 90:10 to 60:40 (% by weight).

21. A composition as claimed in claim 19 or 20, wherein the component C is present in an amount of from 0 to 20 parts by weight per 100 parts by weight of the sum of components A and B.

22. A composition as claimed in claim 19 substantially as herein described with reference to any of the Examples.

23. A process for the production of acid-protonated aqueous coating compositions as defined in Claim 19, wherein part of component A is ground with pigments, fillers, corrosion inhibitors, lacquer auxiliaries and/or organic solvents and subsequently mixed with the other constituents.

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